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ROTATIONAL ENERGY TRANSFER IN HIGHLY VIBRATIONALLY
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WISCONSIN UNIV-MADISON DEPT OF CHEMISTRY F F CRIM
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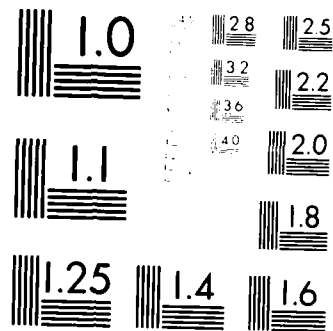
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evolution of individual rotational states observed in the double resonance studies provides level-to-level energy transfer rate constants when analyzed using an iterative fitting scheme which incorporates scaling relations among the rate constants.

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ROTATIONAL ENERGY TRANSFER IN HIGHLY VIBRATIONALLY EXCITED

HYDROGEN FLUORIDE AND DEUTERIUM FLUORIDE

(Contract No. N00014-79-C-0415)

(Principal Investigator: F. Fleming Crim, University of Wisconsin)

Scientific Problem

Molecular energy transfer is a fundamentally and practically important process that has received and continues to merit substantial experimental and theoretical study. One of the most important practical manifestations of the importance of collisional energy transfer is in chemical lasers, where the details of the energy redistribution pathways control the performance of the device and where mathematical models require a substantial amount of dynamical and kinetic information. Such models are central to understanding and improving the performance of these lasers. On a more fundamental level molecular energy transfer experiments are important as sources of data for comparison with theoretical descriptions of inelastic scattering. In particular, detailed data on rotational and vibrational energy redistribution in collisions are the means of testing classical and quantum mechanical calculations that predict the variation of rates and pathways with excitation level or quantum number. Despite the rather extensive body of data on vibrational energy transfer that now exists on molecules in low vibrational levels, the theoretical descriptions remain incomplete, particularly for molecules in which long range forces play a significant role.

Experimental studies of molecular energy transfer in hydrogen and deuterium fluoride provide the data for practical models of chemical

laser and for comparison to theoretical descriptions. Our approach is to use laser excitation of overtone vibrations to prepare molecules in individual rotational states of highly vibrationally excited hydrogen fluoride or deuterium fluoride and to use laser double resonance to monitor the populations of individual quantum states during the subsequent collisional relaxation. These experiments measure individual relaxation rate constants and provide the means of unravelling the detailed vibrational and rotational relaxation pathways.

Recent Progress

Our Office of Naval Research funded activities have been in three broad areas during the last two years: rotational relaxation, vibrational relaxation, and hardware development. In these experiments, a 6 ns pulse of light from a Nd:YAG/dye laser or the near-infrared pulse generated by stimulated Raman scattering of the dye laser light excites an overtone vibration of hydrogen fluoride, and continuous infrared radiation from a HF chemical laser probes the populations of individual vibrational-rotational states of the excited molecule or its collision partner. A transient digitizer captures the time-evolution of the amplification or absorption of the probe laser radiation as it passes through a cell collinearly with the excitation beam, and extensive averaging of the signal yields reliable population and rate information with a time-resolution of about 20 ns. The following sections discuss the recent experimental results and hardware development work separately.

Collisional Energy Transfer

One of our primary goals in studying the vibrational relaxation of highly vibrationally excited hydrogen fluoride has been to unravel the details of the collisional energy transfer pathways. In particular, we have been determining the relative importance of vibration-to-vibration (V-V) and vibration-to-translation, rotation (V-T,R) energy transfer for the lower vibrational levels of hydrogen fluoride. The former shuttles vibrational energy from the initially excited molecule into the vibration of the collision partner,



while the latter leaves the collision partner in the same vibrational state and deposits energy in translations and rotations of the two molecules



The anharmonicity of hydrogen fluoride makes the first process endothermic while the second is exothermic. The V-V energy transfer becomes increasingly endothermic as the vibrational level increases, but the V-T,R transfer becomes less exothermic at higher vibrational levels. The double resonance technique allows us to monitor the collision partner in order to distinguish the two pathways.

Previous work using the time-evolution of the transient ionization and absorption of light from the probe laser, operating between the $v=2$ and $v=1$ vibrational levels of HF, following pulsed excitation of HF($v=2$) shows that about 60% of the relaxation occurs by the V-V energy transfer route. We have now begun exploring the relative importance of these two pathways in higher vibrational levels by probing the population in $v=1$ subsequent to excitation of HF($v>2$). The key to extracting the relative contributions of the V-T,R and V-V pathways from

these measurements is a knowledge of the relaxation kinetics in the lower vibrational levels. Thus, we use the rate constants and branching ratios that we have determined for $v=2$ in analyzing the data for $v=3$ and then use these results in analyzing higher levels. Our measurements on $\text{HF}(v=3)$ and $\text{HF}(v=4)$ show that the fractions of the relaxation proceeding by V-V energy transfer are about 0.45 and 0.1, respectively. The trend of a decreasing fraction of V-V energy transfer with increasing vibrational level is consistent with the growing endothermic energy defect at higher vibrational levels. As the V-V process becomes successively more endothermic, it plays a smaller role in the overall relaxation kinetics.

The temperature dependence of the collisional energy transfer rates and the branching between the two relaxation routes is a means of discovering the factors that determine the relative importance of V-T,R and V-V energy transfer. Our recent study of the temperature dependence of the vibrational relaxation rate constant for $\text{HF}(v=2)$ (J. M. Robinson, M. J. Pearson, R. A. Copeland, and F. F. Crim, *J. Chem. Phys.* **82**, 780 (1985)), shows that the rate constant for $v=2$ decreases more slowly with temperature than that for $v=1$, where V-T,R energy transfer is the only observable process, and than those for $v=3, 4$, and 5, where the V-V pathway is observable but has a large endothermic energy defect. Detailed analysis of our data for $v=2$ shows that the weaker dependence on the relaxation rate on temperature arises from the prominence of V-V processes in the relaxation of that level. We infer that the efficiency of V-V energy transfer changes more slowly with temperature than does the efficiency of V-T,R energy transfer as Figure 1, which displays the temperature dependence of the two processes extracted from our analysis, illustrates. The origin of the weaker

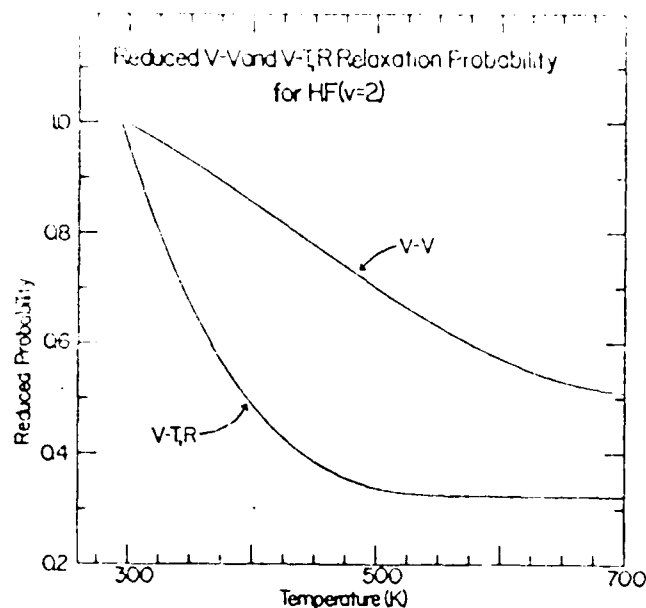


Figure 1

variation of the V-V energy transfer rate constant with temperature is the competition between the decreasing collision duration and the increasing availability of thermal rotational energy. At higher temperatures, the shorter collisions provide less opportunity for long range forces to bring the molecules into close contact for efficient energy transfer, but the larger average rotational energy leads to more collisions in which the internal energy of the collision partner makes up the energy defect for V-V transfer. The competition between these two effects is not so important for the higher vibrational levels where V-V energy transfer contributes less.

Collision partners other than HF are important in chemical lasers, and previously we have used near-infrared laser induced fluorescence to study the relaxation of HF($v=3,4$, and 5) by H_2 , D_2 , CH_4 , CD_4 , and CO_2 . We

have now applied our laser double resonance technique to investigate a potentially very important partner, the hydrogen fluoride dimer (K. J. Rensberger, J. M. Robinson, R. A. Copeland, and F. F. Crim, J. Chem. Phys. (to be published)). At pressures of 50 Torr, HF dimers constitute only one to two percent of the molecules but are significant energy transfer partners if they rapidly relax the vibrationally excited monomer. The decay constants for HF($v=1$) extracted from our measurements over the range of 10 to 50 Torr show curvature that reflects the presence of the dimer. The observed decay constant is

$$\tau^{-1} = k_M P_M + k_D P_D = k_M P + k_D K P^2$$

where k_M and k_D are the monomer and dimer bimolecular energy transfer rate constants, respectively, and P_M and P_D are the corresponding pressures. To a very good approximation, the dimer pressure is $K P^2$ where K is the equilibrium constant and P the total pressure. The data shown in Figure 2 illustrate the influence of the dimer on the pressure

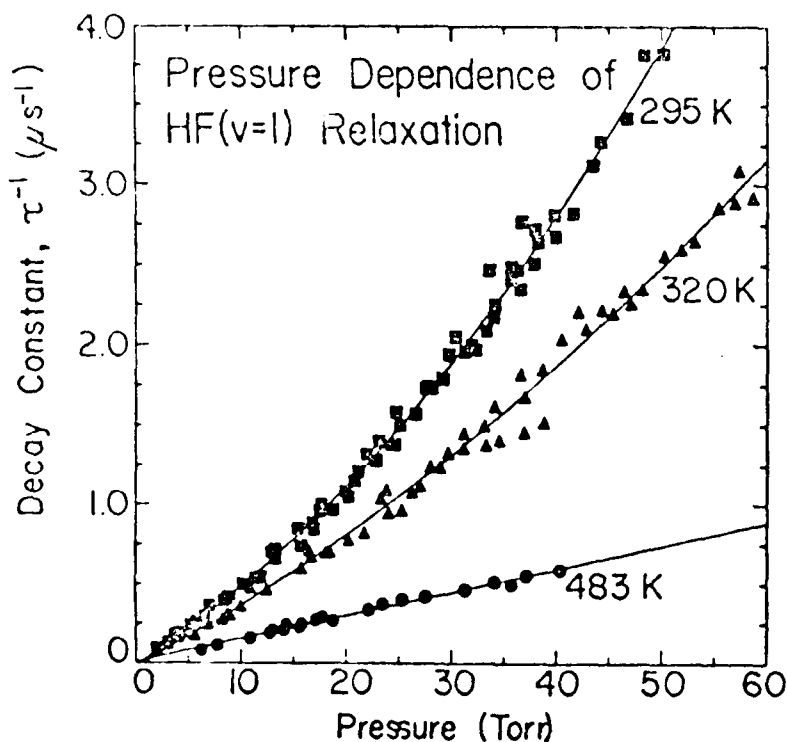


Figure 2

dependence of the observed decay constant. The curvature in the lowest temperature data arises from efficient relaxation of the monomer by the dimer. Fitting these data yields the product of the equilibrium constant and the relaxation rate constant of the dimer by the monomer. The dimer is an extremely efficient collision partner that removes a vibrational quantum from HF($v=1$) in only about five collisions. Our detailed kinetic analysis shows that this very efficient V-T,R relaxation proceeds by a pair of sequential steps in which nearly resonant V-V energy transfer from HF($v=1$) excites the dimer and it rapidly forms two ground vibrational state monomers by vibrational predissociation.

Rotational Relaxation

Our laser double resonance studies of rotational energy transfer are designed to determine the thermally averaged rate constants for relaxation of individual quantum states and to assess the utility of various empirical and theoretically based scaling relations in predicting large numbers of unmeasured rate constants from a few known values. These rate constants and the scaling relations among them have obvious utility in modelling systems, such as chemical lasers, where rotational state populations are controlled by collisional energy transfer. Our extensive experimental studies are described in two papers (R. A. Copeland and F. F. Crim, J. Chem. Phys. 78, 5551 (1983) and J. Chem. Phys. 81, 5819 (1984)) that present the results and apply various scaling relations to the analysis of the laser double resonance data. The two categories of scaling relations that we use are those

based on the energy defect for the rotational energy transfer process, primarily the exponential energy gap and the power law models, and those based on the energy corrected sudden (ECS) approximation. Both of the energy based scaling relations adequately fit our data, which span the combinations of approximately six excitation and six independent probe levels, but do show significant differences in their predictions for the behavior in higher levels that are not part of the data set. The most successful scheme for reproducing our measurements is the ECS approximation model. This model, which includes angular momentum constraints that are absent in those based solely on energy, gives a much better fit to the data for $J=0$ to 6 than the other scaling laws. It is also the most successful in predicting the results for very high rotational levels. The ability to extrapolate these ECS approximation based scaling laws beyond the region over which the parameters were fit is quite promising for models of complex systems.

Hardware Development

The goal of studying vibrational and rotational relaxation in deuterium fluoride using the measurement and data analysis techniques that we have developed for hydrogen fluoride depends crucially on several experimental advances in our laboratory. The two most important of these are stabilization of our continuous chemical probe laser, to permit more extensive signal averaging, and conversion of our laser to operate on molecular deuterium. During the last funding period we have accomplished these goals and assembled an In:Sb detector suitable for use in the wavelength range of deuterium fluoride transitions. We have also acquired experience with longer wavelength red dyes and begun producing several millijoules of energy in the region of 1.8μ by

Intensity Stabilization

The laser stabilizer uses an electrooptic crystal to alter the polarization of the laser light along one axis that is parallel to the transmission axis of a polarization analyzer. An error signal generated by a detector monitoring the laser intensity controls the voltage across the crystal, and, hence, the degree of ellipticity of the polarized beam. This system dramatically reduces fluctuations in the laser intensity below about 100 kHz and makes possible the more sensitive detection and extensive signal averaging required for studying the less favorable deuterium fluoride system. Figure 3 illustrates the dramatic improvement possible with the stabilizer. The figure shows the stabilized signal (top) and unstabilized signal (bottom) over a period

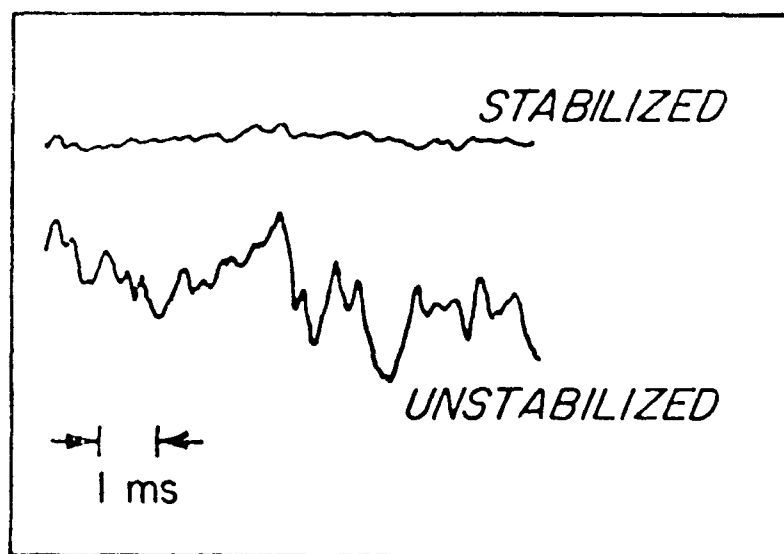


Figure 3

of about 10 ms. (Both signals have the same full scale amplitude.)

laser is an important accomplishment that has resulted from the new measurements on deuterium fluoride.

Our current major development has been converting our HF chemical laser to operate as a DF chemical laser. This involves pumping molecular hydrogen in the $H_2 + F$ pumping reaction with deuterium gas. The laser is less efficient for DF, and our design has been altered by a new, more stable laser cavity that we have designed for this purpose. We have operated the laser on both the $v=2$ to $v=1$ transition and the $v=3$ to $v=2$ transition on seven different rotational lines. Table I summarizes the preliminary performance characteristics of our laser.

TABLE I. DF Chemical Laser Power (mW)

Transition	$v=2 \rightarrow v=1$	$v=3 \rightarrow v=2$
$J=1$	5	-
$J=4$	30	-
$J=5$	38	12
$J=6$	50	30
$J=7$	70	55
$J=8$	55	50
$J=9$	50	45
$J=10$	-	25

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